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## **Recent Advances in Bleaching and Dyeing of Animal Fiber**

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### **ABSTRACT**

Animal fibers, goat-derived as well as wool, camel, alpaca, and angora rabbit, traditionally are bleached using hydrogen peroxide. Peroxide efficiently removes stain. If preceded by a fiber mordanting procedure with ferrous sulfate, peroxide also assists in the depigmentation of these fibers. Even whiter products may be achieved by "full" bleaching, i.e. peroxide bleaching followed by an afterbleach with a reductive agent such as thiourea dioxide. A novel procedure now permits full bleaching in a single bath; residual peroxide from the first step is converted chemically into a reducing bleach by reaction with thiourea. Animal fibers are typically dyed using acid or reactive dye species. Dyestuffs are selected based on washability, brightness desired, and leveling properties of the dye system. In some cases, the single-bath bleaching process can be extended to permit subsequent dyeing in the same bath.

## INTRODUCTION

Usage of animal fiber in textile products is dominated by wool. Nevertheless, problems inherent in processing other animal fibers, such as cashmere and mohair, are similar to those of wool, and the approaches to overcome these problems are essentially the same. This is because the chemical properties of all hair tissue are similar and linked by the protein class they all have in common — keratin, and to the extent that the fibers are pigmented, by the polycyclic aromatic pigments, the melanins.

The focus by the Agricultural Research Service (ARS) on the bleaching and dyeing of animal fibers is on wool. American wool is mainly a by-product of the meat industry, and as such it often contains an excessive amount of stained and pigmented fibers. As a result, its perceived quality and its price are significantly lower than its imported (mainly Australian) counterpart. The objective of the ARS research program is to improve the value of domestic wool, and we have spent some time in particular to develop new technology to bleach stained and pigmented fibers.

Bleaching of wool for pigmentation is targeted at black hair contamination, the incidental black fiber in what typically is an off-white fleece. The only naturally pigmented wool subjected to depigmentation bleaching is Karakul. The same bleaching processes used for pigmented wool are used for other naturally pigmented fibers, such as camel hair or cashmere.

The chemical constituents that cause stain have never really been thoroughly characterized, but they result both from the degradation (thermal, photo-, chemical, and microbial) of keratin protein and from the uptake of foreign substances (including urine, manure, chlorophyll (often from manure), and substances found in the suint (sweat)).

## BLEACHING FOR STAIN

Bleaching chemistry was reviewed thoroughly by Duffield (1986). The most common bleaching is oxidative in nature, and hydrogen peroxide [ $\text{H}_2\text{O}_2$ ] is the most widely used agent for stain bleaching. Formulations with  $\text{H}_2\text{O}_2$  include stabilizers, such as, (ethylene-diaminetetraacetic acid [EDTA], tetrasodium pyrophosphate [TSPP] or sodium silicate, which generally target metal ions that induce free radical decomposition, pH controllers, used to create an acidic environment (pH 5.0-5.5) or more typically an alkaline one (pH 7.5-8.5), and nonionic or amphoteric wetting agents. Time and temperature are set to maximize whiteness and minimize fiber damage. Short times (1-3 hours; 60°C) are preferred for most applications, but overnight runs at lower temperatures are not uncommon for bleaching of stock. In addition to the bleaching of stock, yarn, and fabric,  $\text{H}_2\text{O}_2$  sometimes is added to the last scouring bowl and the stock is dried and baled without further rinsing. Bleaching then takes place in the bale during subsequent storage. Excessive heat buildup in the bale, however, can induce fiber damage.

Reductive bleaching may be used alone as a substitute for oxidative bleaching, but its use is mainly confined to afterbleaching following  $\text{H}_2\text{O}_2$  treatment. The most widely used reductive bleach, though not the best, is sodium hydrosulfite ( $\text{NaO}_2\text{SSO}_2\text{Na}$ ; also known as dithionite, hyposulfite, and sulfoxylate). Following bleaching and rinsing, the fiber is treated with a little  $\text{H}_2\text{O}_2$  to stem residual sulfurous odors.

More favored as reductive bleaches are derivatives of sulfinic acid ( $\text{H}_2\text{SO}_2$ ), all of which are thought to act by decomposition to a fleeting but reactive species, free sulfinate ion. The most common such derivative is sodium hydroxymethanesulfinate ( $\text{HOCH}_2\text{SO}_2\text{Na}$ ; sodium

formaldehyde sulfoxylate), but a newcomer now gaining favor is thiourea dioxide ( $\text{H}_2\text{NC}(=\text{NH})\text{-SO}_2\text{H}$ ; formamidinesulfinic acid).

The most effective bleaching regimens for stain incorporate both an oxidative and a reductive bleaching step and are referred to as "full" bleaching. Such full bleaching is normally a two- or three-step process carried out in separate baths. Industry, however, typically avoids full bleaching, and relies only on oxidative bleaching; the gains from extra whiteness, it concludes, do not offset the added expenses of preparing and heating an additional bleach bath.

In a series of recent reports (Arifoglu and Marmer, 1990a, 1990b; Arifoglu et al., 1990, 1992; Arifoglu and Marmer, 1992a; Cardamone et al., 1992; Marmer et al., 1992, 1993; Cardamone and Marmer, 1993), patents and patent applications (Arifoglu and Marmer, 1990c, 1991, 1992c, 1992d, 1992e, 1993a, 1993b), we at ARS have reported on the development of new approaches to full bleaching that integrate the processes into single-bath procedures. In the ARS process, residual  $\text{H}_2\text{O}_2$  from the initial oxidative bleaching is utilized in a quick chemical reaction that converts the bath into a reductive medium. When thiourea is added to the peroxide bath under controlled conditions, thiourea dioxide is produced, and reductive bleaching ensues.

The reaction proceeds by the interaction of thiourea with two moles of  $\text{H}_2\text{O}_2$  under acidic conditions to form formamidinesulfinic acid (thiourea dioxide). Subsequent hydrolysis under neutral or alkaline conditions then yields urea and the reducing species -sulfinate ion. We routinely follow the course of this reaction by measurement of the redox potential. The residual peroxide bath measures +200 to +400 mV. After thiourea addition and a 10 minute residence time at pH 4.5, the pH is adjusted to above 7. Only then is there a sharp drop in redox potential, to -600 to -700 mV.

<sup>13</sup>C NMR spectroscopy (Arifoglu et al., 1992) and empirical observations led us to recommend using less than the stoichiometric amount of thiourea to H<sub>2</sub>O<sub>2</sub> (0.31:1.0 instead of 0.50:1.0), and later studies (Cardamone et al., 1992; Marmer et al., 1992, 1993) showed that whiteness was still vastly superior to peroxide bleaching even when about 30% of the residual H<sub>2</sub>O<sub>2</sub> is discarded before addition of thiourea. The ARS process, relative to conventional peroxide bleaching, showed minimal fabric damage, inconsequential tensile strength losses, and similar elastic moduli (resistance to elongation) and extension at break (extensibility). Fabric handle (wool challis fabric) was assessed using the Kawabata Evaluation System (KES-F; Kawabata, 1980). Results indicated that the ARS bleaching produced fabric with a softer, more flexible, and smoother feel than seen from conventional bleaching.

### BLEACHING FOR PIGMENTATION

Bleaching for pigmentation involves the selective decomposition of melanin pigment granules in the interior of the fiber. Industry uses one variation or other of the process first reported by Laxer and Whewell (1955) and then perfected by Bereck (1985), which involves the selective mordanting of pigmented fibers by ferrous sulfate. The fiber or fabric is first treated with FeSO<sub>4</sub> in the presence of a reducing agent (phosphorous acid [H<sub>3</sub>PO<sub>3</sub>], hypophosphorous acid [H<sub>3</sub>PO<sub>2</sub>]) to prevent oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>. Following rinsing (sometimes in the presence of a chelating agent such as EDTA or nitrilotriacetic acid [NTA]) to remove the bulk of the FeSO<sub>4</sub>, small amounts of Fe<sup>2+</sup> remain adsorbed specifically to the melanin granules. Subsequent treatment of the fibers with H<sub>2</sub>O<sub>2</sub> causes decomposition of the melanin pigment. The localized reaction on melanin is a free radical one, superimposed on the non-radical and nonselective interaction of H<sub>2</sub>O<sub>2</sub> with stain components.

Bleaching of pigmented animal fibers was reviewed by Knott (1990). This process or its variations is used to bleach not only wool, but other pigmented fibers as well (including cashmere, mohair, alpaca and camel hair, and Angora rabbit hair). Often, only a lighter color is desired from the starting brown fibers, such as might be done to bleach naturally brown camel hair to what the public regards as the camel hair color. Nevertheless, if the bleached goods are to be dyed to a pastel or some medium shades, then bleaching is necessary to assure a white product.

Full-bleaching can be tied into the Bereck process. A particular advantage is the elimination of traces of any orange-colored  $\text{Fe}^{3+}$  species (from the mordanting) by reduction to soluble  $\text{Fe}^{2+}$  (Arifoglu and Marmer, 1990a, 1990b, 1991, 1992c, 1992e, 1993b) during the reduction step of full bleaching.

The ARS single-bath full bleaching process works very well in this situation. The orange-colored species are especially prevalent in bleaching 100% naturally pigmented fibers.

## DYEING

Dyeing of animal fibers is accomplished by a variety of dye classes. Most common are the so-called acid dyes. These dyes are solubilized in water by virtue of their sulfonate groups. "Level dyeing" acid dyestuffs have good leveling properties, but poor washfastness. They are applied at pH 2.5-3.5. Their palette may be considered bright. "Premetallized" dyes (1:1 or 1:2 complexes with Cr, Fe, Co, etc.) show good washfastness, but give a dull palette. The 1:1 complexes have better leveling properties than the 2:1, but are applied under highly acidic conditions (pH 2.0-2.2) rather than neutral, causing problems with fabric handle. Premetallized

dyes are under environmental scrutiny because of their heavy metal content, and they are unstable in the presence of bleaching agents. "Milling" dyes show the brightest palette of all the acid dyestuffs, but their leveling properties are not good.

Coming into vogue are reactive dyes. These dyes are more expensive than their predecessors, but they offer the unique advantage of covalent bonding with the substrate. Such dyed fibers are very stable to laundering and dry cleaning. Because their leveling properties are not good, they are applied mainly to yarn and stock. These include the vinyl sulfones, monochlorotriazines and alpha-bromoacrylamides.

ARS work on the dyeing of animal fibers has been limited: work in conjunction with bleaching research attempted to extend the single-bath bleaching concept into subsequent dyeing. Most recently, we have been examining the problem of uniform dyeing of blends of wool and chemically very dissimilar cotton; preliminary work shows that derivatizing cotton to make it more similar chemically to wool improves the uniformity of dyeing of this blend.

Early in our research, we showed how effective bleaching prior to dyeing can make a substantial difference to the shade and brightness of pastel-dyed fabrics. The extra whiteness obtained by full bleaching (ARS single-bath or traditional dual bath) is visible to the eye, and so is the difference in color following subsequent dyeing.

The single-bath bleaching concept was expanded to allow dyeing in the same bath subsequent to bleaching. In general, the residual bleach bath is conducive to dyeing: it is already heated, it contains two known dye assists (urea and sulfate) from the breakdown of thiourea dioxide during bleaching, and it already contains a wetting agent that serves as a leveling agent as well. Nevertheless, we cannot tolerate any residual bleaching agent, and this



necessitates bringing the bath back from its latter reductive environment to a near-neutral redox potential prior to addition of the dyestuff. Generally, a small amount of  $\text{H}_2\text{O}_2$  is sufficient to neutralize any remaining reductive bleaching species. Sequential dyeing in the bleach bath promotes rapid uptake of dye at lower temperatures than conventional dyeing. Our only bad experience was with a premetallized dye; uptake was too rapid, leading to unlevel dyeing, and the dye shade was sensitive to the redox balance of the system (Arifoglu and Marmer, 1992b, 1993b; Cardamone et al., 1992; Marmer et al., 1993).

The concept of full bleaching and dyeing in the same bath is not applicable to samples that have undergone bleaching for pigment, particularly when dealing with all-naturally pigmented materials. Too much residual iron is present, and this interferes with the color integrity of the dyestuffs.

There are advantages and disadvantages of the ARS bleaching process. The disadvantages need some attention. Control of pH in the mill may not be an easy task, depending on the level of sophistication of its staff and equipment, even though the system tolerates an error of 1 pH unit at each adjustment. The toxicity of thiourea mandates not only careful handling, but also some monitoring of the baths (Dickinson, 1966) to assure the complete consumption of this reagent. Finally, we are consuming  $\text{H}_2\text{O}_2$  to produce the reductive bath. That prevents the recycling of peroxide into the next bleaching operation. Such recycling is frowned upon by some mills, but practiced by others.

The advantages of using the ARS process, nevertheless, are considerable: excellent whiteness, full bleaching in a single bath, use of thiourea instead of much more expensive thiou-

rea dioxide, removal of residual iron (orange cast) when bleaching for pigmentation, strength retention, soft handle, and potential for subsequent dyeing in the same bath.

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